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FA Report R-1703

DEVELOPMENT OF
HIGH TEMPERATURE-RESISTANT PROPELLANTS

Technical Documentary Report No. RTD-TDR-63-4209

January 1964

AF Flight Dynamics Laboratory
Research and Technology Division
AIR FORCE SYSTEMS COMMAND
Wright-Patterson Air Force Base, Ohio

Project No. 1362, Task No. 136205

Prepared under AF MIPR 33(657)-2-R&D-111
by Hercules Powder Company, Kenvil, N. J.
(FA Contract DA-36-038-507-ORD-3572M)
for Frankford Arsenal, Philadelphia, Pa.
Author: R. L. Simmons

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RTD-TDR-63-4209

FA Report R-1703

DEVELOPMENT
OF
HIGH TEMPERATURE-RESISTANT PROPELLANTS

by

R. L. SIMMONS
(Hercules Powder Co.)
(FA Contract DA-36-038-507-ORD-3572M)

for

FRANKFORD ARSENAL
Philadelphia, Pa.

January 1964

Project No. 1362, Task No. 136205
AF MIPR 33(657)-2-R&D-111

RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
Wright-Patterson Air Force Base, Ohio

FOREWORD

The research work in this report was performed by Hercules Powder Company, Kenvil, New Jersey, under Frankford Arsenal Contract DA-36-038-507-ORD-3572M. The program was managed by Frankford Arsenal, U.S. Army Munitions Command, Philadelphia, Pennsylvania, for the Air Force Flight Dynamics Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio, under AF MIPR No. AF 33(657)-2-R&D-111.

This research is part of a continuing effort to obtain propellant actuated devices (PAD) with high temperature capability for crew emergency escape systems for flight vehicles, which is part of the AFSC's Applied Research Program 750A, Mechanics of Flight. The Project No. 13 1362, "Crew Escape for Flight Vehicles," and the Task No. is 136205, "Propellant Actuated Devices Research." Capt. D. R. Barron, of the Flight Dynamics Laboratory, was the Program Engineer.

While the bulk of the work described herein was performed at the Hercules Powder Company's plant in Kenvil, N. J., further evaluation of propellant, including ballistic testing in standard PAD, was performed at Frankford Arsenal, Philadelphia, Pa. The technical supervisor of this contract was M. Visnov, of the Propellants and Explosives Section, Frankford Arsenal.

The author, R. L. Simmons, and Hercules project personnel, including J. H. Godsey, S. E. Sweeney, W. P. Freese, and M. Brauer, collaborated with Frankford Arsenal personnel throughout the program.

ABSTRACT

Trimene Base was found to be a more effective curing agent for potassium perchlorate/Hycar 4021 propellants than DMP-30 and sulfur. Propellant HES-6573 utilizing this approach performed satisfactorily in M73 PAD cartridges in firings from -65° F to 400° F.

Hycar 1051 was successfully crosslinked with triallyl cyanurate, but the resulting propellant binders did not provide increased heat resistance over the straight Hycar 4021/Trimene Base system. Triallyl cyanurate did not crosslink readily with Hycar 4021 and high weight losses resulted from vaporization of TAC during high temperature storage.

Propellants with silicone and fluorocarbon binders possessed superior heat resistance to the Hycars, but lacked energy. Carbon black and powdered aluminum were added to these propellants to boost the impetus, but without success. A slight improvement was noted only with aluminum in Fluorel, a fluorocarbon.

Potassium nitrate was investigated as a chlorine-free inorganic heat-resistance oxidizer in a Hycar 4021 binder, but none of the compositions would ignite. The addition of powdered aluminum and boron did not aid combustion.

Cyclotetramethylene tetranitramine (HMX) was found to have promise as an organic heat resistant oxidizer in a Hycar binder where it gave greater impetus than potassium perchlorate; however, burning rate was considerably slower. None of the HMX propellants exhibited enough heat resistance to meet the 400° F objective, but one composition, HES-6616, showed potential 300° to 350° F resistance.

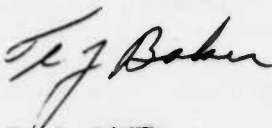
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Limited studies were made for processing the extrudable Hycar propellants in grains up to one inch in diameter and in fine granulations as small as 0.04 inch diameter for fast burning applications. The key to good quality grains appears to be the removal of mixing solvent prior to extrusion.

PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

FOR THE COMMANDER:



T. J. BAKER
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RTD-TDR-63-4209

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INTRODUCTION

This is the final report under Contract DA-36-038-507-ORD-3572M, which was awarded to Hercules Powder Company in August 1960 by Frankford Arsenal. This contract was for the development of solid propellants for propellant actuated devices (PAD) which would perform reliably after withstanding -65° to 400° F soak temperatures for a minimum of four hours. These propellants were to be processible by commercial means (extrusion) into small, gun-type grains, including monopropellant and multipropellant geometries. In addition, attempts were to be made to combine processing, thermal stability, and ballistic objectives to meet the performance requirements of the M73 PAD cartridge.

The primary objective of the work reported here was the solution of problem areas uncovered in the original effort under this contract. A secondary objective was the limited exploration of propellants, as described above, with the additional parameter of evolving noncorrosive combustion products.

During the initial contract effort, several solvent-extruded composite propellant types were developed. The most successful of those which met contract objectives were based on potassium perchlorate oxidizer and polyacrylic elastomer binder. An interim report* covered results of this work.

Several problems were encountered during the initial contract studies which influenced the direction of the work and required a further concentration of effort in certain areas. These were:

1. Improvement of processibility of propellant fuel-binder copolymers with maximum symmetrical triazine derivative content.
2. Increase in impetus of solid propellants containing fluorocarbon and silicone fuel-binders.
3. Formulation of propellants with high temperature-resistant organic oxidizers with favorable oxygen balance.
4. Formulation of propellants with high temperature-resistant, nonchlorine-containing inorganic oxidizers.

*J. H. Godsey and W. P. Freese, "Development of High Temperature Resistant Propellants, Summary Report No. 1," ASD-TDR-62-1085 (FA Report R-1683), June 63.

Two additional areas of investigation were later included by agreement with contractor technical personnel. These were:

5. An improved cure for the polyacrylic binder propellants, to prevent adhesion between grains when stored in PAD cartridges at 400° F. (This condition, detected in further evaluation at Frankford Arsenal, was considered undesirable although the performance of adhered grains in 400° F-exposed M73 cartridges was satisfactory.)

6. An extension of propellant grain sizes to determine the minimum and maximum grain geometries obtainable in these composite propellant formulations by the commercial extrusion process.

The technical approaches employed for the various areas of investigation were:

1. Improve polyacrylic rubber binder cure by substitution of better curing agent and change in cure temperature-time schedule.

2. Incorporate maximum amounts of triallyl cyanurate in extrudable rubber systems to determine if high temperature resistance was significantly increased.

3. Increase impetus of extrudable fluorocarbon and silicone binder propellants by increasing flame temperature and gas output. Inclusion of powdered metal, such as aluminum, was the approach for flame temperature increase; addition of carbon to the formulations was the approach to increase gas output.

4. Investigate cyclotetramethylene tetranitramine (HMX) as a high temperature-resistant organic oxidizer.

5. Investigate potassium nitrate as a chlorine-free inorganic oxidizer.

To enable further concerted work in these areas, this effort was extended in the form of Modification No. 2 to the contract. This final report covers studies conducted under the contract extension during the period July 1961 through August 1962.

EXPERIMENTAL SECTION

Processing

Two different mixers were used to make the propellant samples, a Bramley-Beken mixer of 2-quart capacity for the experimental mixes and a Baker-Perkins sigma-blade ten-pound mixer for the production batches. The procedure for mixing was to mix the rubber with methyl ethyl ketone solvent, incorporate curing agents or crosslinker, and incorporate the oxidizer. A 2-inch diameter vertical press was used for extrusion. Strands were cut into grains with a McKiernan-Terry small arms cutter. The equipment, with the exception of the Bramley-Beken, is the same as that used for double base propellants. Extrusions through dies of 0.50 inch or larger were made with either very low solvent concentrations or without solvent. One mix of Hycar 1051 and TAC (HES-6671) was attempted without success using only the TAC as plasticizer.

After granulation, the propellant was dried (or cured) for two days at 55° C and glazed with 0.1 percent graphite.

Testing

Heat of explosion was determined in a Parr calorimeter of 22 cu in. capacity, following the procedure of NAVORD-OD-9375 with one exception - one atmosphere of nitrogen rather than 25 atmospheres.

The density of the grains was determined according to MIL-STD-286, method 510.1.1, but using cyclohexane instead of distilled water. This modification yields more accurate measurements based on tests with high energy double base propellants.

The ballistics of each formulation were assessed in a 180-cc closed bomb using standard Hercules procedures. The loading density was 0.0945 gm/cc when a charge weight of 17 grams was used. The reference propellant was HES-5808.7C, a propellant composed of AP in a cellulose acetate binder capable of withstanding 200° F for long periods without appreciable decomposition.

The two parameters measured in the closed bomb were relative quickness and relative force. These are normally measured on an equal weight basis, but when propellant density differences are great, it is advantageous to load the charges on an equal volume basis. The results obtained in this way are distinguished in the

tables by "W" for weight and "V" for volume. In most instances the rubber-based propellants were denser than the reference, and compare more favorably on a volume basis. This is more meaningful for volume-limited systems such as PAD cartridges.

Weight losses upon exposure to different temperatures were measured by placing samples, weighing from 10 to 20 grams, in an oven for a designated period and cooling overnight in a desiccator.

DISCUSSION OF RESULTS

Improvement in Polyacrylic Binder (Hycar 4021) Cure

Because the adhesion between grains of HES-6468 (KP in Hycar 4021), after exposure to high temperatures, detracted from an otherwise suitable propellant, it was necessary to resolve the problem. It was thought that the Hycar 4021 might not be completely cured with the tertiary amine DMP-30 and sulfur curing agents used. Better ones were sought and, of the several tried, Trimene Base (a reaction product of ethyl chloride, formaldehyde, and ammonia) proved to be the best and appeared to crosslink with the Hycar 4021.

The degree of crosslinking depended on the curing temperature; higher temperature cures gave less swelling in acetone tests (Table 1). Increased crosslinking was also shown with larger amounts of Trimene Base (HES-6573). Adhesion between grains of HES-6573 was still present, though it was considerably decreased when exposed to 400° F in M73 PAD cartridges. Propellants formulated with KP, Hycar 4021, and Trimene Base are shown in Table 2. Also shown are two similar propellants using AP instead of KP. These were not tested extensively (HES-6568 and HES-6575).

Other curing agents tried with KP/Hycar 4021 were MgO in HES-6585 and complex mixtures containing ZnO, sulfur, stearic acid, PbO, Captax and butyl zimate in HES-6600 and HES-6601. All of these proved to be ineffective.

TABLE 1. Qualitative Crosslinking Tests of
KP/Hycar 4021/Trimene Base Propellants

<u>Propellant HES No.</u>	<u>Trimene Base (%)</u>	<u>Cure (°F)</u>	<u>Reaction in Acetone</u>
6566	0.46	250	Considerable swelling
6566	0.46	400	Moderate swelling
6566	0.46	250/400	Slight swelling
6573	1.00	130	Very slight swelling

TABLE 2. Hycar 4021 Propellants Cured with
Trimene Base

HES No.	6566	6573	6635	6568	6575
Oxidizer	KP	KP	KP	AP	AP
Percent oxidizer	84	84	72	84	84
Percent Hycar 4021	15.54	15	26.24	15.54	15
Percent Trimene Base	0.46	1	1.76	0.46	1
Observed H _{ex} (cal/gm)	1386	1400*	-	1465	-
Observed density (gm/cc)	1.95	1.90	1.79	1.70	-
Weight loss after four hours at 400° F (%)	-	1.74	1.32	-	-
Closed bomb**					
RQ (%) W	80	92	64	114	-
RF (%) W	55	54	55	104	-
RQ (%) V	95	102	103	118	-
RF (%) V	76	63	129	118	-

*Estimated

**HES-5808.7C reference equals 100% RQ and 100% RF

W - weight basis

V - volume basis

Incorporation of Increased Triallyl Cyanurate (TAC)
in Rubber Binders

During the latter part of the first year's effort, formulations of Hycar 4021 with TAC were found to be heat resistant and of considerable promise. Hycar 4021, being a copolymer of 95% ethyl acrylate and 5% chlorovinyl ether, by weight, is almost

completely saturated and the reaction with TAC was probably more physical than chemical.

The purpose of TAC was to serve as a crosslinking agent to get a three-dimensional network with the heat-resistant cyanurate structure included but without the extreme brittleness that a TAC polymer exhibits alone. To facilitate crosslinking, it was necessary to use an unsaturated polymer that would have more reactive sites. Hycar 1051 (a butadiene-acrylonitrile copolymer) and butyl rubber (a copolymer of isobutylene and isoprene) were two likely binders that not only were unsaturated, but were free of halogens, which would make them useful binders for nonhalogenated oxidizers. Estimated structures and thermochemical data for these compounds are shown in Appendix I.

Propellant HES-6614 was formulated with KP/Hycar1051/TAC and found to be highly crosslinked if cured correctly. The binder was soluble in acetone after curing at 200° F and only slightly soluble when cured at 300° F. A sample cured at 500° F was unaffected by acetone. Three more formulations were made with increasing amounts of TAC to gain more heat resistance, but troubles were encountered in processing propellant with more than eight percent TAC (Table 3) because of tackiness.

TABLE 3. Hycar 1051 Propellants Crosslinked with TAC

HES No.	6614	6621	6658	6671
Percent KP	84	84	75	73.2
Percent Hycar 1051	12	8	12.25	12.2
Percent TAC	3.8	8	12.25	14.6
Percent Catalyst	0.2	+0.4	0.5	+0.1
Observed H _{ex} (gal/gm)	1327	1320	-	-
Observed density (gm/cc)	1.97	2.02	1.89	-
Weight loss after five hours at 400° F (%)	1.59	3.00	-	-
Closed bomb*				
RQ (%) W	101	75	45	-
RF (%) W	66	60	61	-
RQ (%) V	120	88	61	-
RF (%) V	94	82	86	-

*HES-5808.7C reference equals 100% RQ and 100% RF

W - weight basis

V - volume basis

The optimum amount of TAC for proper crosslinking with Hycar 1051 is estimated to be 48% TAC/52% Hycar 1051, by weight, according to reactions outlined in Appendix I. Qualitatively, this has not been borne out by observing weight losses after exposure to high temperature (Table 3). Weight losses generally increase as the concentration of TAC increases and probably reflect the vaporization of TAC, which has a boiling point of 324° F. The substitution of Hycar 4021 for Hycar 1051 does not affect weight loss at 3.8 percent TAC level (HES-6484 in Table 4) and when TAC is removed completely, the weight loss diminishes (HES-6468 in Table 4).

TABLE 4. Hycar 4021 Propellants with Earlier Curing Agents

HES No.	6395	6468	6484	6396*
Composition (wt %)				
KP	80.00	84.00	84.00	-
AP	-	-	-	80.00
Hycar 4021	19.40	15.55	12.00	19.40
TAC	-	-	3.80	-
DMP-30	0.40	0.35	-	0.40
Sulfur	0.20	0.10	-	0.20
Luperco ATC	-	-	0.20	-
Observed H_{ex} (cal/gm)	1268	1380	1425	1277
Observed density (gm/cc)	1.89	1.81	2.03	1.70
Weight loss after five hours at 400° F				
	0.55	0.90	1.13	13.33
Closed bomb data**				
RQ (%) W	63	82	86	74
RF (%) W	61	57	51	92

*Excessive weight loss precludes use at 400° F.

**HES-5808.7C reference equals 100% RQ and 100% RF.

W - weight basis.

Examination of the weight loss as a function of time at constant temperature for a KP/Hycar 4021/TAC propellant (HES-6484) reveals that the weight loss increases rapidly for the first hour, then increases at a constant but lesser rate for the remainder of the heating period (Figure 1). Weight losses during the linear rise period averaged 0.08 percent per hour, indicating that use of the first two hours as a curing period will yield lower weight losses during high temperature storage. The effect of just such a high temperature cure on the ballistics of HES-6484 in the closed bomb was

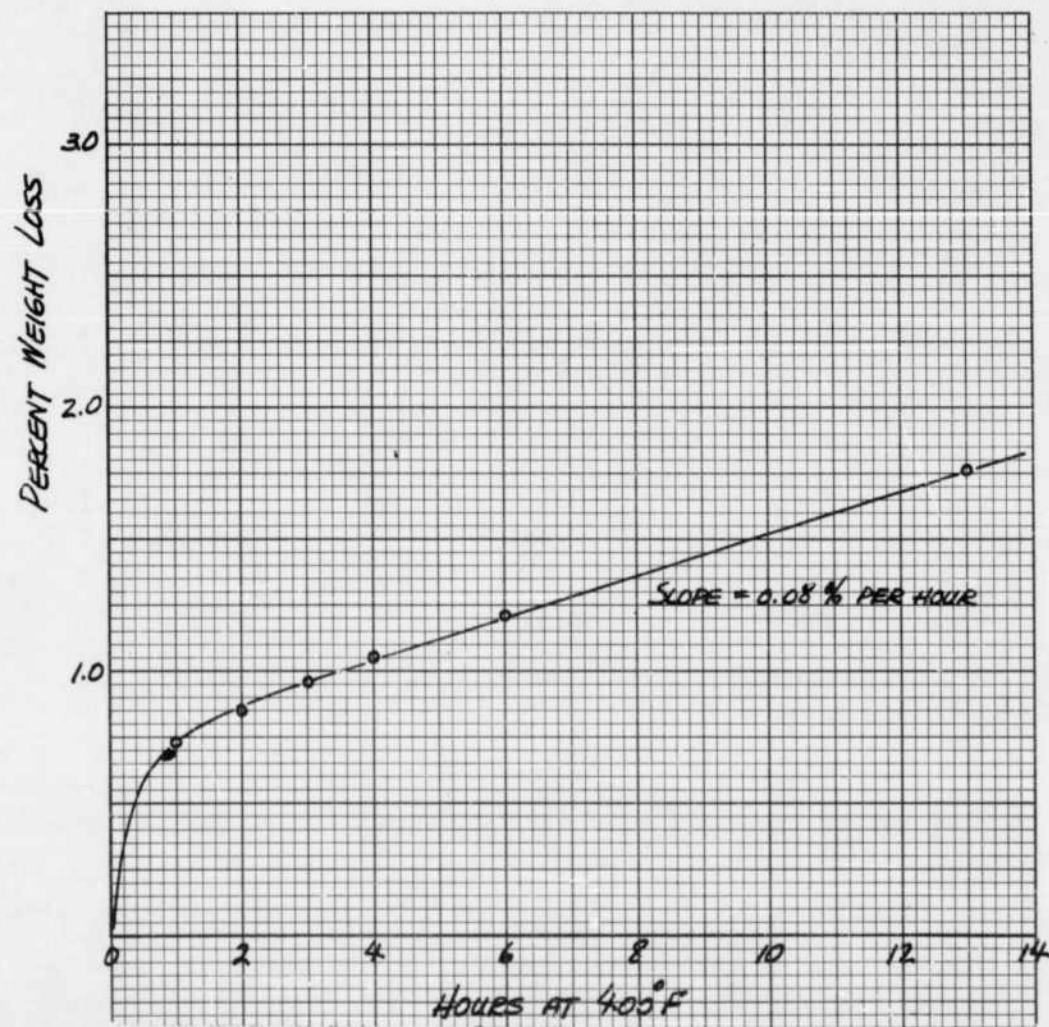


Figure 1. Weight Loss of HES-6484 at 400° F

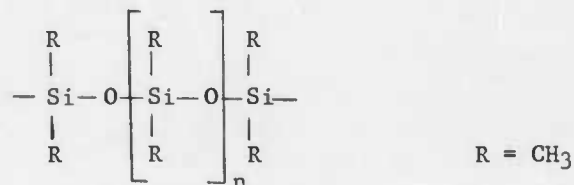
was found to be nil (Table 5). While this type of curing was investigated only for a Hycar 4021/TAC system where crosslinking was not expected, it may be useful in improving the high temperature-resistance of Hycar 1051/TAC propellants where excess TAC boils off to give high weight losses.

TABLE 5. Effect of High Temperature Cure on
HES-6484 Closed Bomb Ballistics
(HES-5808.7C = 100% RQ and 100% RF)

	<u>Equal Weight Basis</u>		<u>Equal Volume Basis</u>	
	<u>% RQ</u>	<u>% RF</u>	<u>% RQ</u>	<u>% RF</u>
Uncured	86	51	108	78
Cured two hr at 400° F	97	54	111	77
Four hr at 400° F after cure	92	52	109	77

Studies to Increase Impetus of Silicone Binder Propellants

In spite of the superior heat resistance of silicone polymers with the general structure



they were difficult to process via solvent techniques because they were so weak and soft. Also, silicones are not particularly energetic.

Four formulations were made during the second year to overcome these deficiencies (Table 6). Cab-O-Sil (colloidal silica) was tried as a reinforcing agent in the two formulations HES-6615 and HES-6625, with some improvement; however, the binder was still too weak to permit scale up.

Carbon black and powdered aluminum were tried in the three composition HES-6612, 6615, and 6625, to increase the flame temperature and/or gas output.

TABLE 6. Silicone Binder Propellants

HES No.	6571	6612	6615	6625	6412*
Percent KP	84	62.8	62.8	62	84
Percent Silastic 433	15.60	-	-	-	15.1
Percent Silastic 440	-	16.2	13.4	29	-
Percent Al	-	20.4	20.4	-	-
Percent carbon black	-	-	-	5	0.5
Percent Cab-O-Sil	-	-	3.0	3	-
Percent DiCup R	-	0.6	0.4	1	-
Percent Puperco CSF	0.40	-	-	-	0.4
Observed H _{ex} (cal/gm)	-	1596	1660	974	1575
Observed density (gm/cc)	-	1.93	1.93	1.68	2.05
Weight loss after five hours at 400° F (%)	-	-	1.10	1.80	-
Closed bomb**					
RQ (%) W	-	-	70	47	119
RF (%) W	-	-	44	47	46
RQ (%) V	-	-	88	50	-
RF (%) V	-	-	63	50	-

*Shown for comparison

**HES-5808.7C reference equals 100% RQ and 100% RF

W - weight basis

V - volume basis

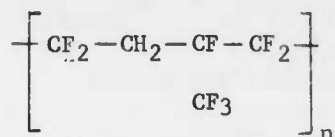
Of the two formulations that contained aluminum, one (HES-6612) yielded no ballistic information because the propellant grains balled together into one large lump. The other (HES-6615) showed no increase in energy in the closed bomb over an unmodified composition (HES-6412). The net effect appeared to be a decrease in burning rate, as indicated by the relative quickness in the bomb.

Carbon black in HES-6625 also showed no evidence of increasing impetus in the closed bomb and burned even slower than the aluminum-modified propellant. Further work with silicones was suspended after these tests.

Studies to Increase Impetus of Fluorocarbon Binder Propellants

The previous fluorocarbon binder propellants made with Viton B elastomer were easy to mix and extrude, but lacked sufficient

strength to hold together during granulation. Another elastomer, which was similar to Viton B chemically but which had more suitable mechanical properties, was Fluorel KX-2141, a copolymer of perfluoropropylene and vinylidene fluoride



Three formulations were made of KP/Fluorel modified with carbon black and aluminum to increase the energy level. Carbon black in HES-6628 gave a slight increase in both the energy and burning rate, according to closed bomb data (Table 7). The burning rate of an unmodified Kp/Fluorel propellant (HES-6624) was too low to measure in the bomb.

Powdered aluminum produced an increase in energy and burning rate in both of the formulations tried (HES-6629 and HES-6676). None of the three modified Fluorel propellants appeared to be suitable for further testing, and further work was discontinued.

TABLE 7. Fluorocarbon Binder Propellants

HES No.	6628	6629	6676	6624*
Percent Fluorel KX-2141	34.69	19.82	10.32	16.52
Percent KP	50.00	56.00	82.50	80.00
Percent LD-214	0.42	0.24	0.13	0.20
Percent carbon black	8.00	-	-	-
Percent aluminum	-	20.00	5.00	-
Percent MgO	6.89	3.94	2.05	3.28
Observed H_{ex} (cal/gm)	920	1829	1720	1562
Observed density (gm/cc)	2.06	2.06	-	1.94
Weight loss after five hours at 400° F (%)	0.87	0.30	0.19	0.31
Closed bomb**				
RQ (%) W	22	49	43	Low
RF (%) W	42	52	40	38
RQ (%) V	35	61	84	-
RF (%) V	61	71	52	-

*Unmodified composition for comparison.

**HES-5808.7C reference equals 100% RQ and 100% RF

W - weight basis

V - volume basis

Formulations with Chlorine-free Inorganic Oxidizers

Potassium nitrate (KN) was selected as a promising inorganic oxidizer, free of halogens and possessing a reasonably high thermal stability (melting point of 639° F). A propellant (HES-6594) was formulated with KN in a Hycar 4021 binder cured with Trimene Base. Processing was trouble-free; however, the propellant could not be ignited in the calorimeter or closed bomb, even at two different loading densities.

Powdered aluminum and boron were tried as combustion aids at a concentration of three to seven percent, but without success. Two propellants HES-6626 and 6627 (Table 8) would still not ignite in the calorimeter or closed bomb. Doubling the igniter in the bomb only gave partial burning. All work on this type of propellant was stopped.

TABLE 8. Potassium Nitrate Propellants

HES No.	6594	6626	6627
Percent KNO ₃	84	69	63
Percent Hycar 4021	15	22.5	32
Percent Trimene Base	1	1.5	2
Percent Boron	-	-	3
Percent Aluminum	-	7	-
Observed density (gm/cc)	1.71	1.53	1.54
Weight loss after five hours at 400° F (%)	-	1.50	1.33

Formulations with Organic Oxidizer

For an all organic, high temperature-resistant oxidizer, cyclotetramethylene tetranitramine (HMX) was chosen for evaluation. It has a high melting point (527° F) and good thermal stability, i.e., the 5-second explosion temperature is 621° F and the weight loss at 400° F is 1.48 percent after five hours.

HMX was formulated with Hycar 4021 into propellant HES-6570 (Table 9). Processing was trouble free, and the ballistics in the closed bomb indicated that it had sufficient energy, but the burning rate was low and the weight loss at 400° F was higher than desired.

TABLE 9. HMX Propellants

HES No.	6570	6616	6630
Percent HMX	80	84	87.5
Percent Hycar 4021	20	-	11.72
Percent Hycar 1051	-	15.8	-
Percent Luperco ATC	-	0.2	-
Percent Trimene Base	-	-	0.78
Observed H_{ex} (cal/gm)	857	840	984
Observed density (gm/cc)	1.63	1.59	1.66
Weight loss after five Hours at 400° F (%)	7.33	91.5	Burned
Closed bomb ^a			
RQ (%) W	66	51	81
RF (%) W	103	101	109
RQ (%) V	74	56	87
RF (%) V	116	121	120

*HEX-5808.7C reference equals 100% RQ and 100% RF

W - weight basis

V - volume basis

The binder was changed to Hycar 1051 cured with Luperco ATC, and the solids loading increased to 84 percent, by weight (HES-6616). Processing was still trouble free. From the ballistics in the closed bomb, impetus or energy had been increased slightly, but the rate, or quickness, had dropped. The weight loss after five hours' exposure to 400° F was excessive (91.5 percent). A study of the weight loss at lower temperatures showed that 350° F was the limit.

The binder was changed to Hycar 4021 cured with Trimene Base, and the solids loading increased to 87.5 percent (HES-6630). The result was a slight increase in energy and a significant increase in burning rate. During weight loss tests, the samples caught fire within an hour at 400° F. Small scale stability tests showed no incompatibility between HMX and any other of the ingredients. No explanation can be given for either the excessive weight losses or burning behavior, but it is suspected that the decomposition products of either HMX or Hycar may be responsible.

Extension of Grain Sizes

Fine Grain Studies

For application in high temperature-resistant propellant-actuated cable cutters and similar devices, attempts were made to process the polyacrylic binder propellants in extremely fine granulations. During the first year's contract effort, a small sample of an ammonium perchlorate Hycar 4021 propellant (HES-6405.8) had been extruded with some difficulty in a Bullseye cut (0.038 in. diameter, 300 cuts/inch). In limited tests at Frankford Arsenal, this propellant had performed satisfactorily in a cable cutter. The choice of ammonium perchlorate (AP) propellant was dictated by closed bomb firings of AP and KP propellants with similar binder and granulation against double base Bullseye propellant as standard. As expected, these had shown AP considerably superior in quickness and force over the KP propellant. Although thermal stability study had shown that the AP propellants would not meet the 400° F temperature resistance, there was still an area of application for 200° to 300° F resistance which the commonly used double base Bullseye propellant would not meet.

Attempts were repeated to process an AP/Hycar 4021 propellant (HES-6575), in a slightly coarser granulation (0.053 in. diameter, 98 cuts/inch). A small amount was obtained with some difficulty. Attempts to duplicate the propellant on a larger scale failed repeatedly. The propellant strands broke easily and were very tacky during granulation.

An HMX propellant, HES-6616, which had a history of being easy to process, was granulated 300 cuts/inch, but when compared to Bullseye in closed bomb tests, was too slow to be recorded. Another propellant mix was tried wherein AP was substituted for HMX (HES-6665), but problems similar to those encountered with HES 6575 arose during granulation, and the mix was discarded. Partial replacement of HMX by AP was tried (HES-6673) in an effort to alleviate processing difficulties, but it was not successful. Some improvement in physical strength of the strands was noted, but the tackiness resulting from solvent in the binder was too great, and the mix was discarded. All four of the compositions are given in Table 10.

Large Grain Studies

Attempts were made to extrude grains of half inch and one inch diameters of two of the KP/Hycar 1051/TAC propellants, HES-6614 and -6621, but the details for trouble-free processing were not completely worked out. The key to good quality grains appeared to be the removal of mixing solvent prior to extrusion and a slow cure at gradually increasing temperatures.

TABLE 10. Compositions for Extruded Fine Grain Studies

HES No.	6575	6616	6665	6673
Percent AP	84	-	84	69
Percent HMX	-	84	-	15
Percent Hycar 4021	15	-	-	-
Percent Hycar 1051	-	15.8	15.8	15.8
Percent Trimene Base	1	-	-	-
Percent Luperco ATC	-	0.2	0.2	0.2

Excess residual solvent caused the grains to be soft and tacky, while quick curing at high temperatures distorted the grains. A cycle of one week of ambient rest followed by a week at 200° F gave reasonably good cures with HES-6614. Truly solventless extrusions combined with a slow cure cycle appear to be necessary for reproducible, high quality grains of half inch diameter or larger.

Thermal Decomposition of Various Oxidizer/Binder Combinations

Selected propellants containing KP and AP in Hycar 4021 and HMX in 1051 were subjected to various temperatures to determine the weight loss behavior. KP in Fluorel was similarly tested. The results, shown in Figures 2, 3, and 4, indicate that of the two major constituents in the propellant, the one with the least heat resistance governs the heat resistance of the system. For instance, KP is more resistant than Hycar 4021, and a propellant composed of these two (HES-6468) exhibits the stability of Hycar 4021. AP, on the other hand, is less resistant than Hycar 4021, and propellant HES-6405 exhibits the stability of AP. This also seems to hold true for KP and Fluorel, where KP is thought to be less resistant to heat than Fluorel. In Figure 5 it is seen that HES-6616, being composed of HMX in Hycar 1051, decomposes faster than HMX. This appears to be a result of interaction between oxidizer and binder at high temperature.

Re-evaluation of Performance by Closed Bomb

To further evaluate the best propellants developed to date under the contract, the following eight propellants were retested in the closed bomb under constant conditions to obtain data free of variations in the numerous firings over the contract period: HES-6468, HES-6484, HES-6573, HES-6614, HES-6616, HES-6621, HES-6635, and HES-6658. The results are given in Table 11.

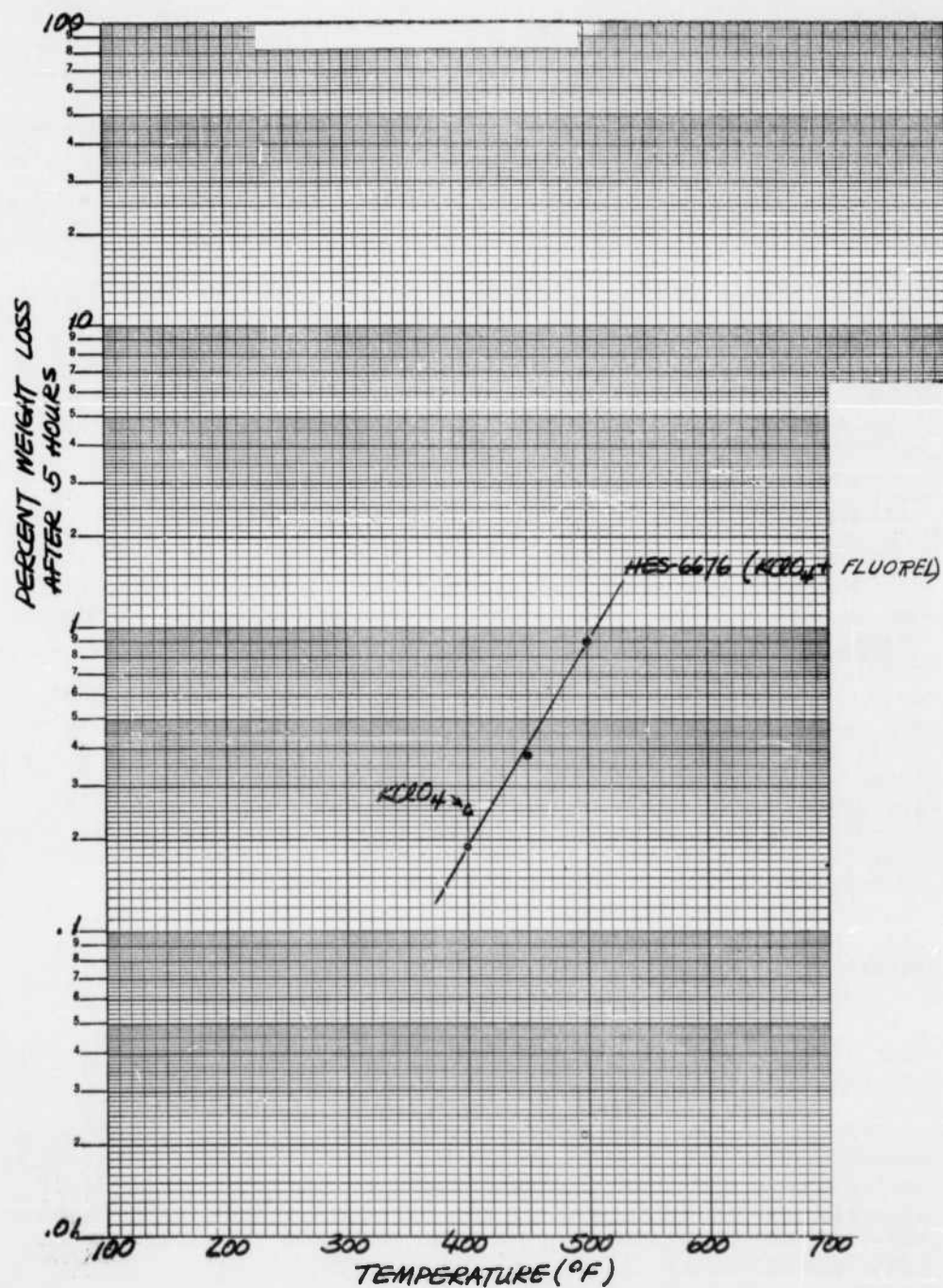


Figure 2. Effect of Temperature on Weight Loss of KP/Fluorocarbon

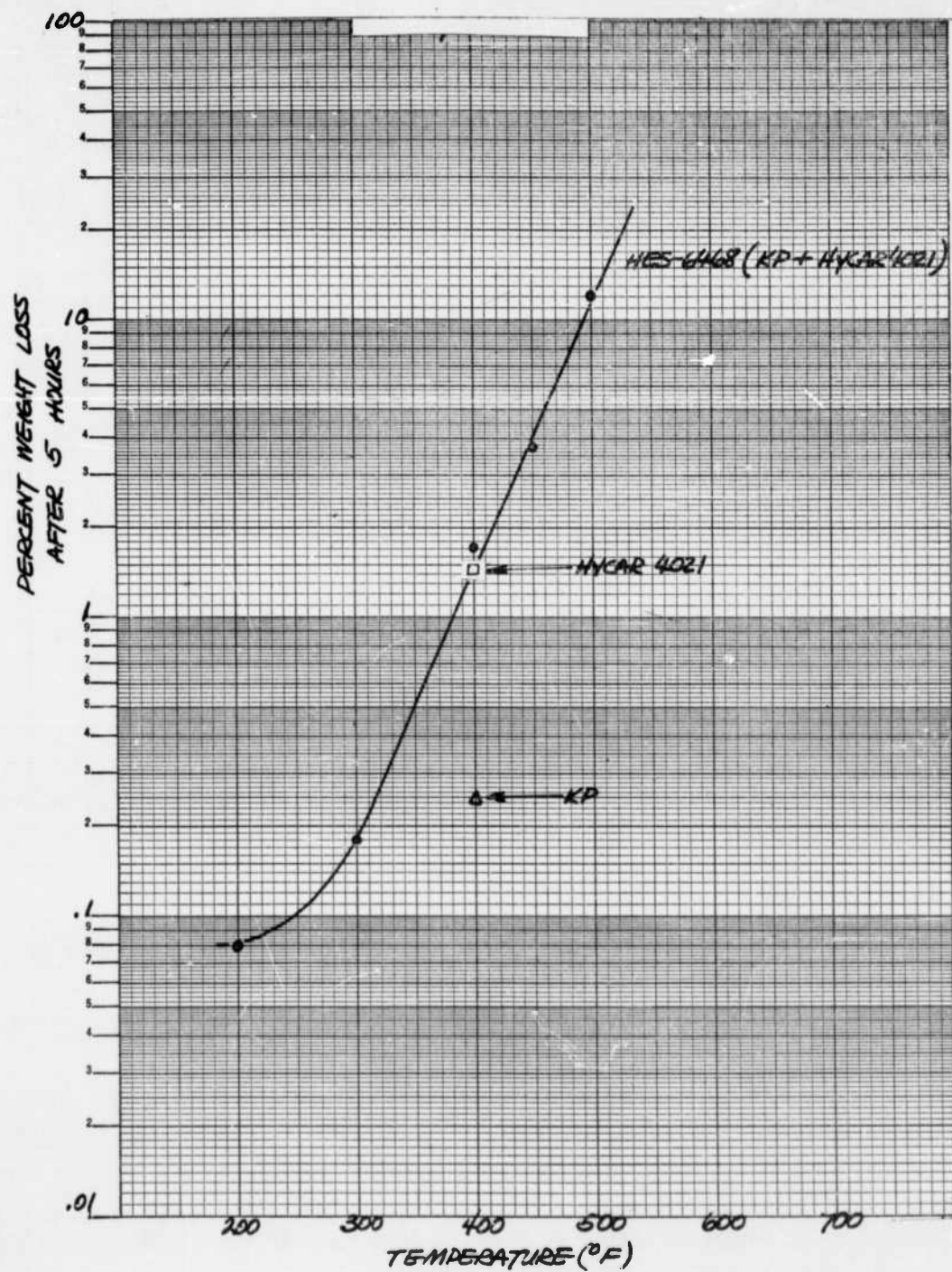


Figure 3. Effect of Temperature on Weight Loss of KP/Hycar 4021

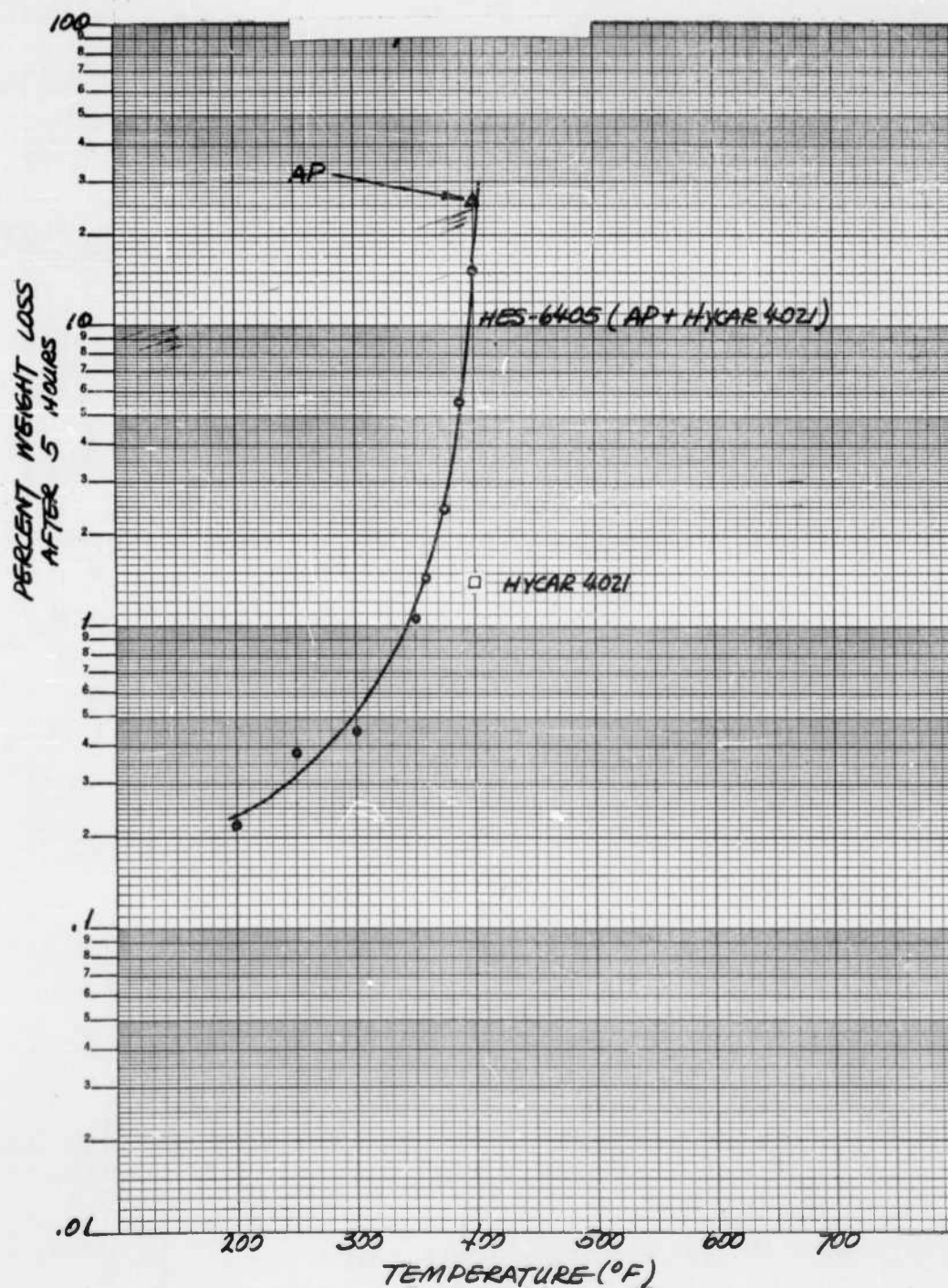


Figure 4. Effect of Temperature on Weight Loss of AP/Hycar 4021

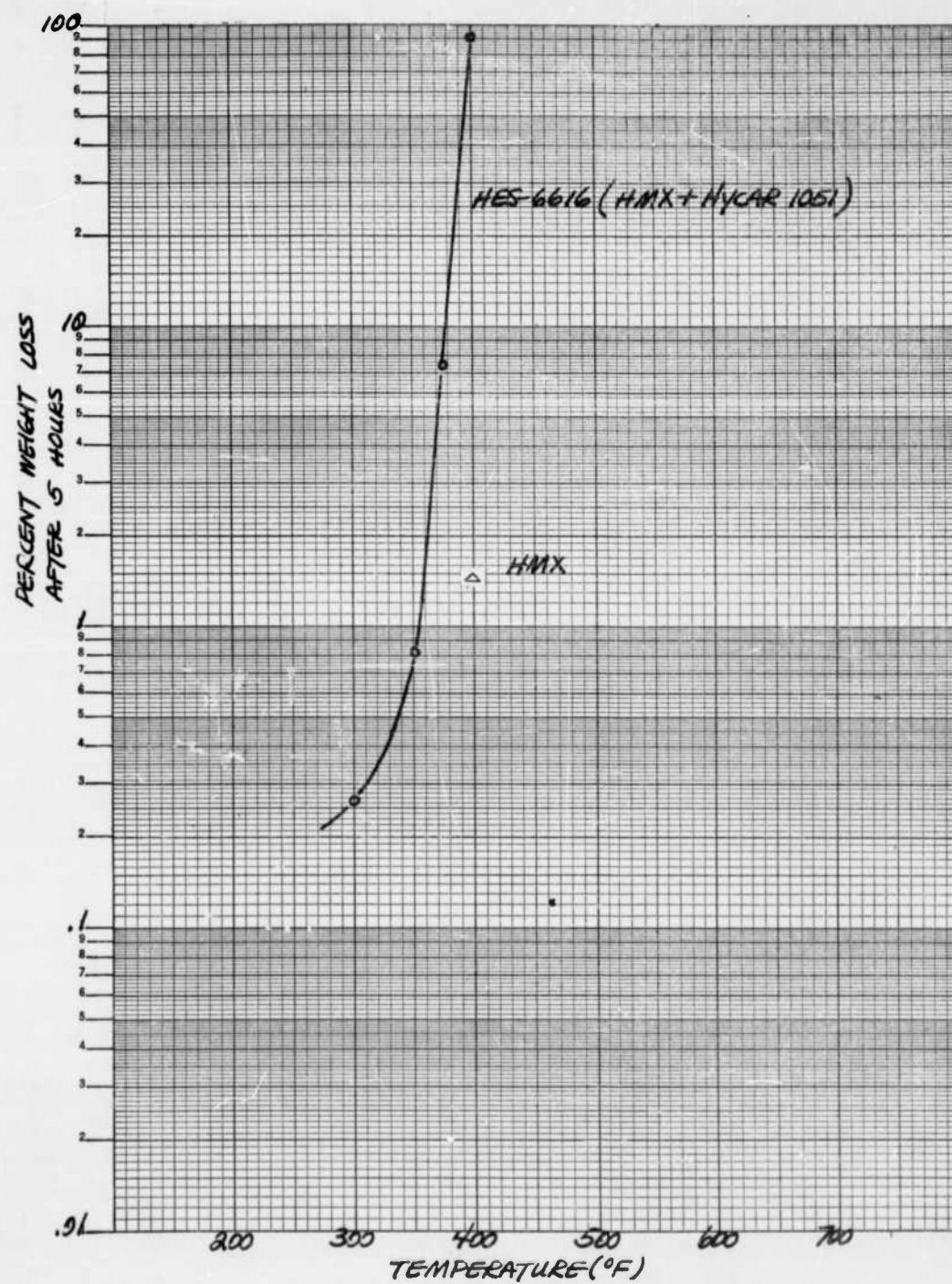


Figure 5. Effect of Temperature on Weight Loss of HMX/Hycar 1051

TABLE 11. 180 cc Closed Bomb Data

HES No.	Constant Weight Charge			Constant Volume Charge				
	Charge (gr)	RF (%)	RQ (%)	Max Pressure (psi)	Charge (gr)	RF (%)	RQ (%)	Max Pressure (psi)
6468.1A	17.0	57	82	6,578	24.0	79	100	8,892
6484.1A	17.0	51	86	6,068	23.7	78	108	8,746
6573.1	17.0	54	92	6,403	20.1	63	102	7,122
6614.1	17.0	66	101	7,855	22.7	94	120	10,580
6616.1	17.0	101	51	11,991	18.6	121	56	13,591
6635.1B	17.0	55	64	6,558	31.7	129	103	14,459
6658.1	17.0	61	45*	7,265	22.1	86	61*	9,712
6621.1	17.0	60	75	7,070	20.3	82	88	9,195

*This low value is attributed to closed perforations.

The standard used for comparison was HES-5808.7C at 100% RF and 100% RQ.

Ballistic Evaluation of Hycar 4021/Trimene Base Propellant in M73 Cartridges

Since formulation studies had shown that improved cures of KP/Hycar 4021 propellants were obtained with Trimene Base, a 10-pound production sample of HES-6573.1B propellant, containing 1 percent curing agent, was sent to Frankford Arsenal for further ballistic evaluation. This propellant was loaded into M73 cartridges with finely granulated USF potassium nitrate-boron igniter and fired in the M3 initiator specification test fixture after exposures from -65° to 400° F for various time periods. Round-by-round data are shown in Table 12 (Appendix II). Firings at the various temperatures were satisfactory.

CONCLUSIONS

The requirements for extrudable high temperature-resistant small grain propellants for PAD can be met with propellants composed of high loadings of KP in Hycar 4021 or Hycar 1051 rubber binders. Hycar 4021 is best cured with Trimene Base, and Hycar 1051 is best crosslinked with TAC.

These propellants can be processed via commercial solvent techniques using the same equipment that is used for the manufacture of double base propellants. The grain size can be changed at will to obtain different burning characteristics - small, fine granulations for rapid burning or larger grains of one inch diameter for slower applications.

The substitution of AP for KP offers greater impetus for a given grain geometry, but the heat resistance at 400° F is poor. Substitution of HMX for KP offers more energy, slower burning, and noncorrosive combustion products, but the heat resistance at 400° F is poor.

The use of a fluorocarbon binder, such as Fluorel, rather than Hycar 4021 or Hycar 1051 offers greater temperature resistance but with an unacceptable sacrifice in energy. Addition of a small amount of finely atomized aluminum results in somewhat improved quickness and force, presumably due to increase in flame temperature.

RECOMMENDATIONS

The perchlorate/Hycar propellants represent a new family of composite propellants extrudable in small, gun type geometries for application in propellant actuated devices. It is recommended that

1. Additional research and engineering tests be conducted for the purpose of phasing them into PAD which require heat resistance above 200° F and which can tolerate some chlorine-containing combustion products.
2. Processing studies for these propellants be continued in the direction of solvent-free extrusion (or partial polymerization) for the purpose of extending the range of maximum and minimum grain sizes.
3. The HMX/Hycar propellants be explored further in the interest of developing a heat resistant propellant system with nonchlorine combustion products.

APPENDIX I

STRUCTURE OF PROPELLANT BINDERS

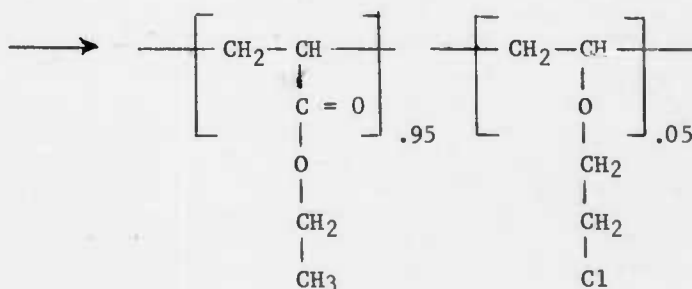
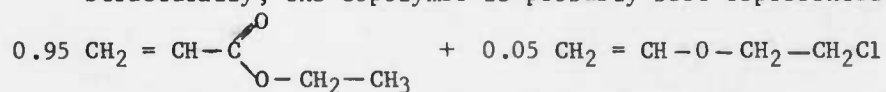
Hycar 4021

Estimated to be a copolymer of 95% ethyl acrylate and 5% chlorovinyl ether with the empirical formula



Molecular weight = 100.44
 Heat of combustion = 6482 cal/gm (calculated)
 6498 cal/gm (observed)
 Heat of formation = -86.48 Kcal/mole (exothermic)

Structurally, the copolymer is probably best represented by

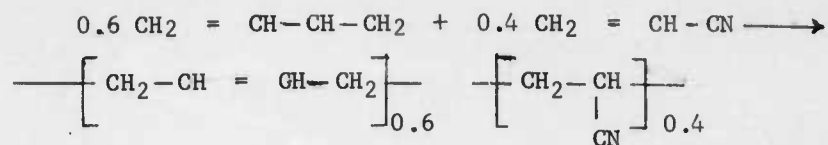


Hycar 1051

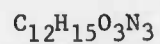
Estimated to be a copolymer of 60% butadiene and 40% acrylonitrile with the empirical formula



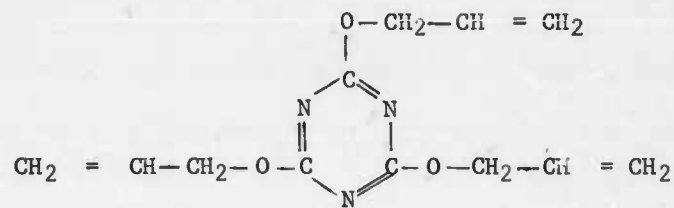
Molecular weight = 53.68
 Heat of combustion = 9896 cal/gm (calculated)
 9593 cal/gm (observed)
 Heat of formation = -28.68 Kcal/mole (exothermic)



Triallyl Cyanurate



Molecular weight = 249.26
 Heat of combustion = 5911 cal/gm (observed)
 Heat of formation = -167.60 Kcal/mole (exothermic)



APPENDIX II

ROUND-BY-ROUND DATA

TABLE 12. Frankford Arsenal Test Firings, HES-6573.1B Propellant in M73 Cartridge/M3 Initiator System

<u>Cartridge Exposure</u>	<u>Firing Temp (° F)</u>	<u>Peak Pressure (psi)</u>	<u>Ignition Delay (ms)</u>	<u>Rise Time (ms)</u>
Unconditioned	70	1440	16	25
		1440	14	20
		1320	16	22
		1480	17	24
		1270	16	21
400° F/4 Hr	70	1290	13	28
		1300	11	24
		1280	12	22
		1500	11	24
		1400	12	24
400° F/6 hr	70	1240	11	31
		1430	13	20
		1300	12	22
		1270	12	23
		1270	13	24
400° F/8 hr	70	1580	10	25
		1540	12	22
		1430	12	22
		1420	9	21
		1400	10	26
400° F/10 hr	70	1300	11	27
		1300	11	24
		1320	9	20
		1230	10	25
		1290	10	23
400° F/12 hr	70	1340	9	20
		1340	10	20
		1390	10	25
		1480	9	22
		1460	10	21
400° F/24 hr	70	1230	17	27
		1230	17	26
		1240	18	20
		1200	19	25
		1200	18	22
350° F/168 hr	70	1340	21	18
		1340	24	21
		1320	25	26
		1180	20	24
		1320	19	25

TABLE 12. Frankford Arsenal Test Firings, HES-6573.1B Propellant
in M73 Cartridge/M3 Initiator System (Cont'd)

Cartridge Exposure	Firing Temp (°F)	Peak Pressure (psi)	Ignition Delay (ms)	Rise Time (ms)
Repeat Firings				
Unconditioned	70	1600	11	21
		1540	13	18
		1470	16	17
		1540	11	15
		1390	11	25
350° F/168 hr	70	1500	10	24
		1330	13	21
		1390	14	22
		1330	14	23
		1300	13	20
350° F/168 hr	-65	1200	11	26
		1140	13	27
		1290	11	23
		1180	12	25
		1040	16	30
350° F/168 hr	-65 (locked shut)	-	Function O.K.	
		-	Ditto	
		-	Ditto	
		-	Ditto	
		-	Ditto	
400° F/24 hr	70	1380	14	16
		1280	13	25
		1240	12	21
		1180	12	18
		1230	14	21
400° F/24 hr	-65	1180	15	21
		1230	12	27
		1380	12	20
		1100	15	24
		1030	24	26
400° F/24 hr	-65 (locked shut)	-	Function O.K.	
		-	Ditto	
		-	Ditto	
		-	Ditto	
		-	Ditto	
Hot Firings				
Unconditioned	70	1400	61 ^a	18
		1060 ^b	58 ^a	25
		1140 ^b	56 ^a	26
		1330	58 ^a	25
		1300	51 ^a	21
400° F/4 hr	400	1450	53 ^a	11
		1350	54 ^a	17
		1230 ^b	53 ^a	15
		1520	51 ^a	15
		1550	53 ^a	15

^aLong ignition delay due to electric glow plug used in 400° F firings
in place of percussion primer.

^bGas leakage through glow plug.

TABLE 12. Frankford Arsenal Test Firings, .25-6573.1B Propellant
in M73 Cartridge/M3 Initiator System (Cont'd)

<u>Cartridge Exposure</u>	<u>Firing Temp (°F)</u>	<u>Peak Pressure (psi)</u>	<u>Ignition Delay (ms)</u>	<u>Rise Time (ms)</u>
Repeat Hot Firings				
Unconditioned	70	1340	58 ^a	19
		1190	56 ^a	24
		1270	56 ^a	18
		1380	56 ^a	23
		1390	50 ^a	19
400° F/4 hr	400	1330	63 ^a	18
		1490	45 ^a	18
		1570	50 ^a	15
		1460	46 ^a	18
		1440	58 ^a	15
Long Term 300° F Exposure				
Unconditioned	70	1280	8	24
		1330	11	24
		1280	8	26
		1280	11	27
		1340	11	28
300° F/4 weeks	70	1340	10	28
		1140	11	25
		1290	9	24
		1120	10	25
		1090	9	28
300° F/4 weeks	-65	1300	12	19
		1340	10	20
		1270	9	23
		1200	9	23
		1240	9	23
300° F/4 weeks	-65 (locked shut)	-	Function O.K.	
		-	Ditto	
		-	Ditto	
		-	Ditto	
		-	Ditto	

^aLong ignition delay due to electric glow plug used in 400° F firings
in place of percussion primer.